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Impedance spectroscopy studies in polymer salt complex films with varying concentrations

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Abstract : We present some results based on impedance spectroscopy and morphology studies on SPE (Solid Polymer Electrolyte). Our host material is polyethylene oxide complexed with ammonium perchlorate [PEO(1–x)-NH_4ClO_4(x)], where x denotes the weight fraction. The Cole-Cole plot shows a semi circle and a spike. The spike is not vertical and may have a curvature. The real part of conductivity shows a power law variation with frequency. This is characteristic of disordered structures, which may also be fractal.

Keywords : Ion conduction, polymer, impedance spectroscopy.

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1. Introduction

In the last thirty years, there has been much interest in finding new solid electrolytes with high ionic conductivity for applications in solid-state batteries. Highly disordered materials, such as polymers, have several advantages over their crystalline counterparts. They have higher ion conductivity at room temperature and are easier to fabricate in different shapes and their conductivity can be varied to some extent by changing the composition. The conduction. mechanism in these materials is not yet fully understood. So this is a very interesting field of study in recent times. Earlier works show that the variation of salt fraction in PEO gives rise to variation in several properties of the polymer film such as dc conductivity, crystallinity, morphology and positron annihilation life time [1–3]. The study of dc conductivity shows that at first the conductivity increases with salt concentration starting from 15wt% up to 17–18 wt(% and starts decreasing thereafter. At all temperatures σ increases with x, with a maximum at x ~0.17. The results show that in polymer electrolytes σ depends on both temperature and salt fraction. Again our works on PALS (positron annihilation life time spectroscopy) show that there is a correlation between τ_{av}, crystallinity and a as x is varied.

Here, τ_{av} is the weighted average of the positron annihilation life times. τ_{av} is minimum at x = 0.18, where σ is maximum and crystallinity is minimum. Figure 1 is a composite representation of σ, crystallinity and τ_{av} *vs* x showing the anomaly in all properties at x ~0.18. We

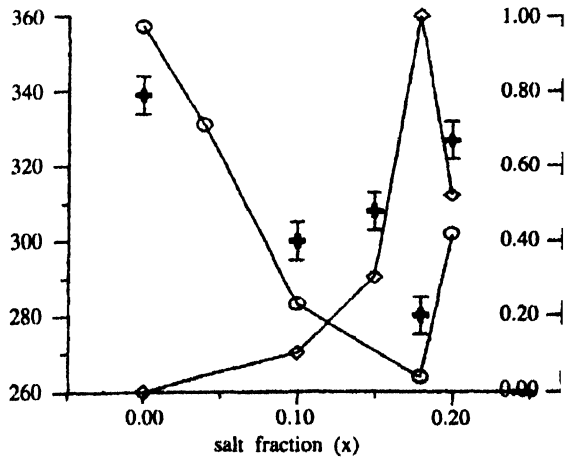

Figure 1. Variation with salt fraction (x) of (a) τ_{av} cross symbol, (b) crystallinity-open circle and (c) ionic conductivity scaled as $\sigma/\sigma_{(x=0.18)}$ -diamond symbol.

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observed further that the morphology of the film shows a striking change at x ~0.18. For lower x fractal aggregates are observed, while above that, polygonal spherulites are formed. In our present work, we have tried to concentrate on impedance spectroscopy studies [4] of the materials. The frequency variation of the ion conductivity and the phase angle contains information about the microstructure of the material. We try to interpret this in the light of earlier observations [5,6].

2. Experimental

2.1. Sample preparation :

The polymer films were prepared by the solution casting technique. Methanol (Spectrochem, 99.9%) was used as the solvent. Fraction x by weight of NH_4ClO_4 (Aldrich, 99.9%) and $(1-x)$ fraction of PEG (Aldrich, MW 6×10^5) were stirred for 12 hr at room temperature (~300 K). Films were cast on a polypropylene dish, dried in air for 5–6 days and then vacuum dried for several hours. x were varied from 0.15 to 0.22.

2.2. Impedance spectroscopy :

The films were taken for spectroscopy studies by placing part of the sample between two spring-loaded electrodes. We have measured the impedance of the samples with the help of an LCR meter (HIOKI 3532-50 LCR HiTESTER) in the frequency range 42 Hz to 5 MHz.

2.3. Morphology :

The morphology of the samples was recorded by a CCD camera. The photographs were taken with magnification approximately 10 times as shown in Figures.

3. Results and discussion

The log of $Y_{re}(S)$ *vs* log of frequency f (Hz) plot, where Y_{re} is the real part of admittance, is shown in Figure 2 for one concentration. For all concentrations the curve consists of approximately two linear regions. The slopes (m) of the linear fit in the high frequency range are given in Table 1. Since the real part of conductivity (σ) is directly proportional to Y_{re}, the slope gives a power law variation [7] of σ with angular frequency ω as given in the equation below :

$$\sigma(\omega) = \sigma_0 + A\omega^m,$$

where σ_0 is the frequency independent part of σ and A is a constant depending upon sample characteristics.

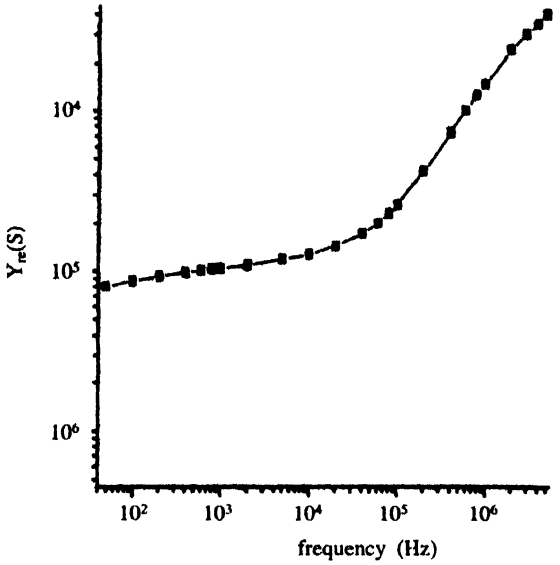

Figure 2. log of Y_{re} (s) *vs* log of frequency f (Hz) plot for salt concentration 19wt%.

Table 1. Variation of the slope of the log τ_{re} *vs* log f plot with salt concentrations.

Concentration of the samples in wt%	Slope (m) in the high frequency region of log Y_{re} vs log f (frequency) plot
15	0.62
16	0.52
17	0.53
18	0.57
19	0.65
20	0.58
21	0.62
22	0.55

The dc conductivity of the samples studied earlier, [2] shows a peak value around concentration 18 wt%. In the previous work [1] conc. of 18 and 20 wt% were studied. Here, the variation is in the steps of 1%. Disordered materials, in particular those with long-tailed distribution of relaxation times or spacing of trapping sites (*e.g.* fractals), show power-law behaviour in conductivity *vs* frequency variation [8]. Jonscher [7] suggested a universal power law for all materials with exponent $m = 0.5$. But later work did not corroborate this [4]. It appears that m may have any value $0 < m < 1$ depending upon the characteristics of the material. Our results show that 'm' is in the range of 0.5–0.6 for all samples with x varying from 15 to 22wt% with no systematic variation with x or any particular anomaly at x ~17–18 wt%. We conclude

that the microstructure on the scale probed by this experiment is essentially similar at all values of x studied. The strong variations in other properties exhibited in Figure 2 are not reflected in the qualitative appearance of the impedance spectroscopy results.

Secondly we took the complex admittance plot (Figure 3), *i.e.* the plot of imaginary part of admittance Y_{im} or B *vs* the real part of Y_{re} admittance or G (also known as the Cole-Cole plot).

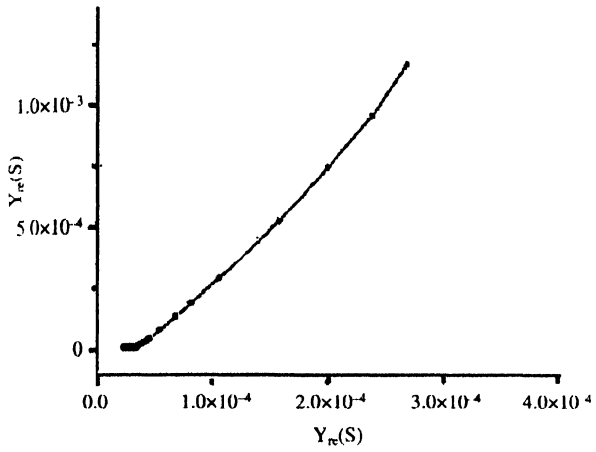

Figure 3. Cole-Cole plot for salt concentration 18 wt%.

For an ideal equivalent circuit consisting of a capacitor and a resistor in parallel, the plot of Y_{im} *vs* Y_{re} is a vertical straight line. For more complicated circuits with lumped circuit elements it has one or more semi-circles followed by a vertical spike (see Macdonald [4], pg. 18).

In our measurements, the curve consists of part of a semicircle, followed by a slanted spike. The slope of the spike for different concentrations lies between 3.5 to 6.7. The spike should be vertical if a simple equivalent circuit with a lumped capacitance and resistance can represent the sample. A slanting or curved spike as obtained by us indicates disorder in the system and has to be represented by a more complex equivalent circuit with distributed elements. We wish to work further in the analysis of the Cole-Cole plot by modeling equivalent circuits using CPE (constant phase element).

The morphology of the films differs from one concentration to another. As observed earlier, in the lower concentrations, smaller sphermulites are observed which turned bigger for higher concentrations. In the region 19wt% to 22wt%, we observed polygon like structures. We present some photographs of the surface of the films in Figures 4 and 5.

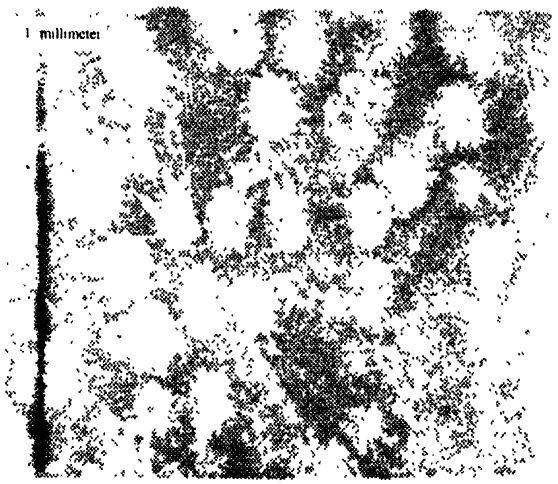

Figure 4. Micrograph of sample with salt concentration 18 wt%, showing fractal aggregates.

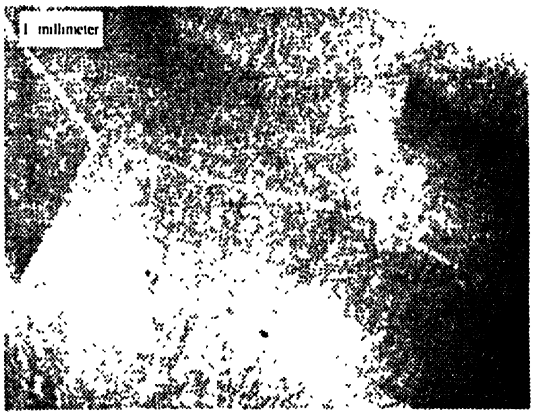

Figure 5. Micrograph of sample with salt concentration 20 wt%, showing polygonal spherulites.

4. Conclusion

We conclude from this study, that the microstructure of the samples seen by impedance spectroscopy does not affect the qualitative nature of the frequency dependence on the ion-condutivity. The power law behaviour observed in Figure 2 is consistent with the fractal nature observed in the samples, but on the length scales, which affect impedance spectroscopy. The structure is similar for all the concentrations studied, hence there is no systematic variation of m with x. It must be kept in mind however, that the impedance spectroscopy results also include effects of the measurement cell geometry. A major problem is to isolate the features, which characterize the sample only.

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